INSTITUTE FOR DIRECT ENERGY CONVERSION

TOWNE SCHOOL

UNIVERSITY OF PENNSYLVANIA

PHILADELPHIA, PENNSYLVANIA

STATUS REPORT

INDEC-SR-15

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GRANT (NSG-316) $N G L - 39 - 010 - 001$

DECEMBER, 1968

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UNIVERSITY OF PENNSYLVANIA
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MANFRED ALTMAN, DIRECTOR

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1. MATERIALS ENGINEERING

Senior Members

Dr. Manfred Altman

Dr. Solomon Pollack

1.1 THERMAL DIFFUSIVITY OF MIXTURES

Senior Investigators: Dr. M. Altman and Dr. K. Sreenivasan

Graduate Student: S. J. Amir

OBJECTIVES

To measure the thermal diffusivity of two types of mixtures:

1. solid mixtures in which the components of the mixtures are both in solid state

2. solid-gas mixtures in which the solid has a certain amount of porosity containing gases like helium or argon

PREVIOUS ACCOMPLISHMENTS

The thermal diffusivities of the following components and mixtures were reported:

1.	CaF_2		INDEC-SR and SR-9
2.	BaF_2		INDEC-SR-9
3.	MgF_2		INDEC-SR-13
4.	$CaF_2 + BaF_2$	(1 to 1 weight)	INDEC-SR-11
5.	$CaF_2 + BaF_2$	(1 to 2 weight)	INDEC-SR-11
.6.	$CaF_2 + BaF_2$	(2 to 1 weight)	INDEC-SR-11
7.	$CaF_2 + MgF_2$	(1 to 1 weight)	INDEC-SR-12, SR-13
8.	$CaF_2 + MgF_2$	(1 to 2 weight)	INDEC-SR-13

The thermal diffusivity was measured over the range of 100 $^{\circ}$c to 1100 $^{\circ}$c using a vacuum furnace.

PROGRESS IN PAST PERIOD

The success of research on determination of thermal diffusivity of porous media at high temperatures depends on the preparation of sample with high porosity, high purity, reasonably uniform pore diameter and uniform density. In the past period many methods of sample fabrication were tried, and a method to make a sample with definite porosity and other characteristics was developed and finalized. Details are given elsewhere in this report.

1.2 TRANSIENT TEMPERATURE RESPONSE OF CYLINDRICAL, COMPOSITE ENERGY STORAGE DEVICES

Dr. M. Altman, Director

Dr. K. Sreenivasan, Post Doctoral Fellow

OBJECTIVES

To develop the analytical solution for the temperature distribution in a cylindrical, composite energy storage device.

PREVIOUS ACCOMPLISHMENTS

None

PROGRESS IN PAST PERIOD

The transient solution to the heat conduction equation in a composite cylinder was developed assuming perfect thermal contact at the interfaces. The solution was used to obtain the temperature response of the energy storage device. Details are shown on pages A1-6 through A1-11.

1.3 EXPERIMENTAL DETERMINATION OF THE THERMOELECTRIC PROPERTIES OF GRAPHITE ALLOYS

Senior Investigator: Dr. S. R. Pollack

Graduate Student: J. J. Curry

OBJECTIVES

To determine the usefulness of quaternary tetrahedral compounds as thermoelectric generator materials.

PREVIOUS ACCOMPLISHMENTS

Reproducible powder metallurgical techniques were developed for fabricating these materials. Electronic equipment was built for measuring thermoelectric power, electrical conductivity, and Hall coefficient as a function of temperature. These measurements were made, and although a high thermoelectric power is obtained, the low value of electrical conductivity prevented usefulness as device material.

PROGRESS IN PAST PERIOD

Analysis of data continues seeking an understanding of the low conductivity.. It was hoped that it could be improved if the mechanism were understood. Unfortunately, we believe the mechanism is alloy scattering, and in order to circumvent this problem, materials fabrication techniques superior to all those tried during the course of this work will have to be developed.

This work was presented at an international conference, and is in preparation for publication.

1.4 SUPERCONDUCTIVITY IN EVAPORATED TUNGSTEN FILMS

Senior Investigator: Dr. S. R. Pollack

Graduate Student: S. Basavaiah

OBJECTIVES

To determine the origin of the Tc enhancement in evaporated tungsten films, and to study the properties of the superconducting films.

PREVIOUS ACCOMPLISHMENTS

The origin of the Tc enhancement was traced to the presence of β-tungsten (A15 structure) which was stabilized during deposition by the presence of oxygen. Control of Tc can be achieved by controlling the oxygen partial pressure, thereby controlling the relative amounts of β to α tungsten. Using tunneling techniques, the energy gap of β-W was measured as a function of Temperature, and found to be adequately described by B.C.S. Theory.

PROGRESS IN PAST PERIOD

This work was completed and two papers were published. The work is continuing with other materials under sponsorship of ARPA.

1.5 BOILING THERMIONIC CONVERTER

Senior Investigator: Dr. Alan M. Whitman

OBJECTIVES

To study the feasibility of a liquid metal collector thermionic converter stabilized by gravity.

PROGRESS IN PAST PERIOD

An experiment was performed with a low boiling point, non-conducting fluid, wherein a stable vapor-liquid interface was maintained with arbitrarily small vapor film thickness. In addition, a thermodynamic analysis of the system was performed which yielded a set of equations suitable for the design of such a device.

2. PLASMA ENGINEERING

<u>Senior Members</u>

Dr. Louis Girifalco

Dr. George L. Schrenk

Dr. Hsuan Yeh

2.1 MHD FLOW IN AN ANNULAR GAP

Senior Investigator: Dr. I. M. Cohen

Graduate Students: W. C. Frazier, J. P. Hanson

OBJECTIVES

To study the fluid mechanics of rotating MHD flows.

PREVIOUS ACCOMPLISHMENTS

Initial experiments were carried out by T. Ebtekar[*] on an old electro-magnet found in the laboratory. This established the orders of magnitude and trends to be expected in the primary variables. With this information, a new magnet was ordered and more careful experiments were prepared.

PROGRESS IN PAST PERIOD

[**] Measurements of the tangential component of velocity as a function of the current driving the magnet and the current through the device were made using a pitot tube. These measurements were taken at a point halfway between the inner and outer electrode, and 0.95 in. below the top electrode. In addition, two velocity profiles from the top electrode to the point 0.95 in. below it were taken at constant device and magnet currents. These profiles showed the tangential component of velocity to be independent of the axial position over this distance (about one sixth of the total length of the device).

The results of the measurements taken as a function of magnet and device current are shown in the attached figure. The pressure differences shown are between the total pressure at the pitot tube, and the static pressure at

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[*]T. Ebtekar, "Flow of a Conducting Liquid in an Annular Gap", Ph.D. dissertation, University of Pennsylvania, May, 1968.

[**] John P. Hanson

the upper insulator at the same radial position as the pitot tube, corrected for the difference in gravity head. The velocity calculation indicator on the figure neglects the magnetic pressure, assumes the r and z components of velocity are small, and that the axial static pressure gradient is only that due to gravity.

The curves in the figure show that the velocity goes as the square root of the device current, if the assumptions concerning the pressure gradient at secondary velocity are born out by further experiments and/or analysis. The line marked "Critical Line" is an overlay of data obtained in other experiments, and are explained more fully in Mr. Frazier's section of the report immediately below.

To determine the nature of the MHD flow, i.e. turbulent or laminar, several devices were constructed and placed in the flow generated in a cylindrical gap. The most promising is a streamlined shape that approximated within 10% NACA 23024 made from stainless steel. Span is 0.50", chord 0.25". A torsion arm was inserted at 0.065" from the leading edge. Angle of attack changes (flutter) was then carried by this torque arm to a light interruption system that measured the changes in angle of attack by proportional voltage from a photocell. Since the major part of the moving mass is in the NACA shape and bearing drag is very low, the system is capable of following fluid incident angle changes on the order of 30 to 50 cycles per second. Computations from the lift-drag data associated with this NACA shape indicate a natural flutter at 40 cps.

Inserted in the flow at 1/3 the distance from the top of the device, and at approximately 2/3 the distance from the inner electrode, the shape was found to flutter at higher frequencies as the tangential velocity was increased. At low velocities, the device was stable and did not flutter -- see included plot.

Additional experiments have shown there to be two vibration modes; i.e., the shape flutters about a zero angle of attack to r tangential and at

an angle of about 30° to this zero line. Further modification of the device will be accomplished to measure these modes accurately.

Frequency of Flutter
vs.
Tangential Velocity for NACA 23024

ONSET OF FLUTTER

β_z field doubled
$\overline{\overline{J}}$ decreased by 10%

Frequency of Flutter cps.

Fluid Velocity M/sec.

Least Square Curve Fit Pitot Tube
Pressure Difference as a Function
of
Magnet and Device Currents
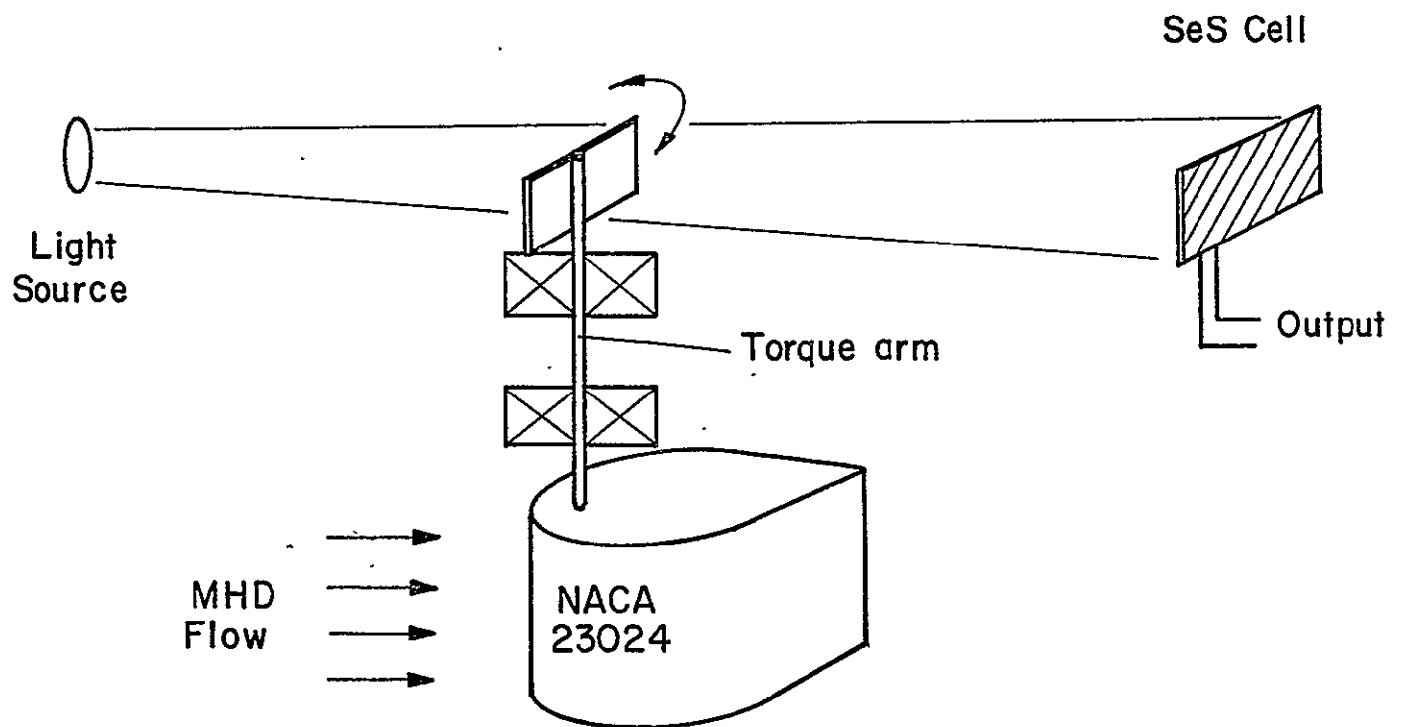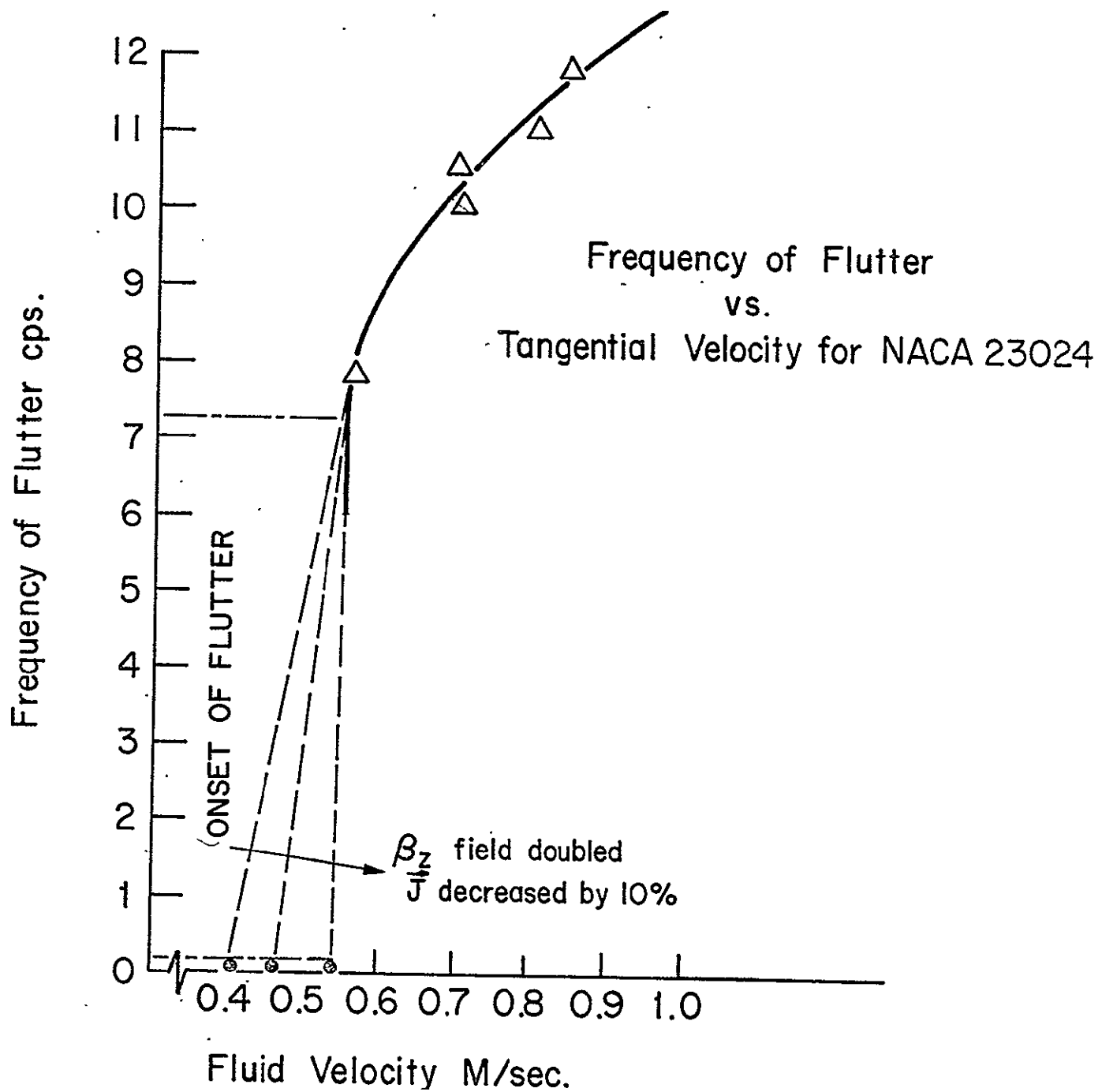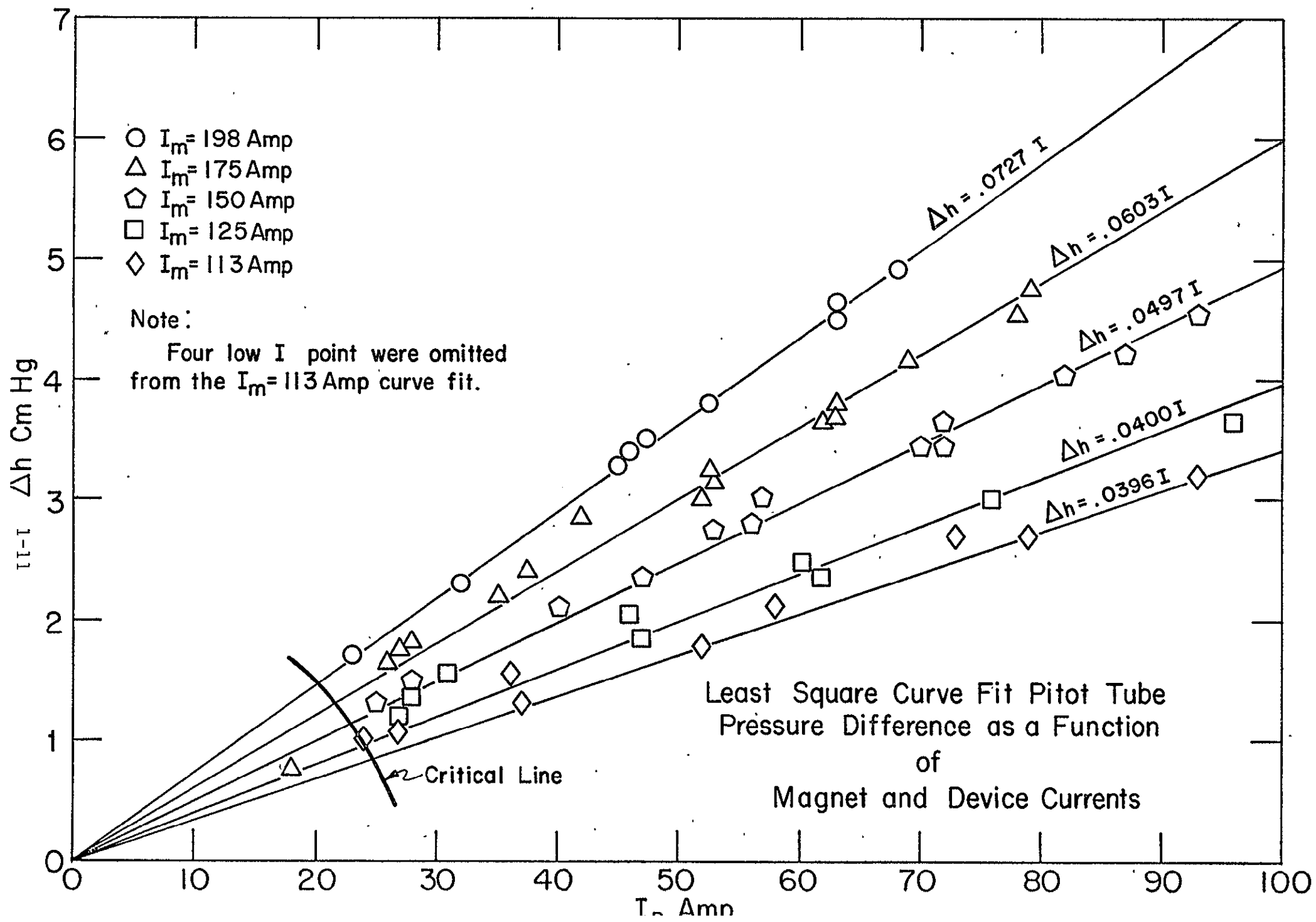
2.2 BASIC SURFACE INVESTIGATIONS

G. L. Schrenk, S. P. Sharma

OBJECTIVES

To study the influence of high fields on surface charge distributions.

PREVIOUS ACCOMPLISHMENTS

Research is in progress to understand the structure of field ion micrographs. In particular, we are trying to understand the varying average intensities of different regions and also the varying intensity of various dots. The regions of varying intensity are rather sharply defined, and are more pronounced in some metals than in others; e.g., in platinum they form one of the most prominent features of the micrograph, while in tungsten, they are barely discernible.

Platinum, as imaged by helium, has been extensively studied. Definite positive effects from the shape of the platinum Fermi surface have been obtained; these results can explain a large part of the structure of the platinum micrograph. These results are limited by the lack of knowledge of the Fermi surface of platinum. This calculation is the first known calculation of high field tunneling probabilities that takes into account the detailed structure of the Fermi Surface of the metal and was the Ph.D. dissertation for Steve Fonash. This calculation was summarized in SR-14.

PROGRESS IN PAST PERIOD

Research is currently under way to understand the varying intensity of the individual dots on a field ion micrograph. We are studying such basic questions as which surface atoms are imaged in a field ion microscope and why.

A quantum mechanical model of the tunneling process has been

constructed; this model treats the variation of surface potential in the plane of the surface as well as the variation perpendicular to the surface. Extensive calculations are in progress. Preliminary results indicate that the amplitude of the variation of the .surface potential in the plane of the surface can have a very significant effect on the tunneling probability. These results are the basis of the Ph.D. dissertation of S. P. Sharma.

2.3 A MATERIALS STUDY OF SILICON SOLAR CELLS

Senior Investigator: S. R. Pollack

Graduate Student: W. H. Becker

OBJECTIVES

To study the structure and properties of contacts to Si with special attention given to titanium-silver contacts used in solar cells in conjunction with the space program.

PREVIOUS ACCOMPLISHMENTS

A survey of the field was made in order to determine the state of understanding. Unfortunately not much work has been done regarding the materials science aspects of the Ti-Ag contacts.

PROGRESS IN PAST PERIOD

Production solar cells from several manufacturers were obtained. Structure and Phase identification work has been started on "good" cells and failures using X-ray diffraction and electron microscopy. Techniques were developed for preparing electron microscopy samples of material under the -contact blisters that occur during failure. Electron diffraction data and transmission electron micrographs have been taken and are currently being analyzed.

2.4 THERMOELECTRIC PROPERTIES OF GRAPHITE COMPOUNDS

Principal Investigator: L. A. Girifalco

Post-doctoral Fellow: S. Sachidanandam

Graduate Student: T. Montelbano

OBJECTIVES

The objective of this work is to examine lamellar alloys of graphite in order to understand the relation of their structure to thermoelectric properties with a view to the possible use of such compounds for thermoelectric applications.

PREVIOUS ACCOMPLISHMENTS

An extend Kronig-Penney model was used for calculations of the electronic band structures of lamellar compounds. The results showed how parameters such as crystal potential and lattice parameters affect the structure, and the semi-conducting or metallic properties of such compounds.

Theoretical work on acoustic phonons in lamellar compounds was performed, and methods of solving the lattice dynamics problem were developed.

Specimens of barium-graphite alloy were prepared. This is a new compound, and its preparation involved many experimental difficulties. The most concentrated compound C_8Ba, is hard and brittle, and has a gold metallic color.

PROGRESS IN PAST PERIOD

The lattice dynamics work was completed and applied to an analysis of the phonon conductivity of graphite alloys. The phonon conductivity was found to be reduced significantly below that of pyrolitic graphite. However, the increases in the electrical conductivity and thermoelectric power, as reported from measurements by other workers on metal-graphite lamellar alloys, give a thermoelectric figure of merit two orders of magnitude below

the commercially viable values. Considering the wide range of values the various samples of graphite are found to have for the electrical parameters, there is reason to believe that purer samples could have much higher figures of merit. The electrical properties are being studied with a view to exploring this possibility.

A paper entitled "Acoustic Phonons in Some Metal-Graphite Lamellar Compounds" is in press with the Physical Review.

The experimental work on barium graphite is continuing.

3. ELECTRO CHEMICAL ENGINEERING

Senior Members

Dr. John O'M. Bockris

Dr. Leonard Nanis

3.1 <u>OVERPOTENTIAL TRANSIENTS ON THE ROTATING DISC</u>

Senior Investigator: Dr. L. Nanis

Graduate Student: Irving Klein

OBJECTIVES

The present problem is an attempt to treat in a rational way a typical electrode for which the mass transport is controlled to permit prediction of electrochemical effects. The rotating disc geometry was found to be ideal for this purpose, and may be used for actual battery electrodes and electrolytes. The present study will accomplish a long desired treatment of combined activation and concentration overpotential transient behavior. Engineering extension to fuel cells and batteries may be obtained by knowledge of the local Nusselt numbers which control mass transport at working electrodes.

<u>PREVIOUS ACCOMPLISHMENTS</u>

A mathematical model has been constructed for the transient redox overpotential decaying from steady state following interruption of galvanostatic conditions. The model includes initial conditions for the individual concentration profiles of an oxidized and reduced species and the time dependent Navier-Stokes equation as applied to a rotating disc geometry. Also, a time dependent functional expression relating overpotential of the total redox system to the concentration of the individual component species has been derived. A rotating disc system has been designed for experimental verification of the analytic treatment, and was made operational. The apparatus was used to examine the steady state behavior of potassium ferricyanide and potassium ferrocyanide redox couples; i.e., the variation of limiting current densities with speed of rotation, and confirmation of theoretical hypotheses was achieved.

PROGRESS IN THE PAST PERIOD

Transient overpotential decay data for the potassium ferricyanide-potassium ferrocyanide redox couple have been obtained. Comparison of the data with theoretical values indicates a good correlation and serves to verify the mathematical analysis upon which the present research is based. Transient overpotential data have been obtained as a function of the following experimental parameters; bulk concentration of the reacting species, bulk concentration of the supporting electrolyte, the rotational speed of the disc, fraction of the limiting current prior to current shutoff. Deviations from the theory occur only when the bulk concentrations of the reacting species are less than $5x10^4$ gmole/liter. The observed anomalies can be explained by considering the possible complexing of the ferricyanide ions with the large excesses of potassium ions created by the presence of the supporting electrolyte, potassium hydroxide.

Work involving the study of transient overpotential buildups at rotating disc electrodes has been initiated. A mathematical model analogous to the one developed for transient overpotential decays has been derived.

3.2 CURRENT AND POTENTIAL DISTRIBUTION IN CYLINDRICAL GEOMETRIES: ENGINEERING APPLICATION TO FUEL CELL DESIGN

Senior Investigator: Dr. L. Nanis

Graduate Student: Wallace Kesselman

OBJECTIVES

The purpose of this research is to derive simple mathematical expressions useful for engineering evaluation of current and potential distributions for common geometries, as encountered in fuel cells or battery design.

PREVIOUS ACCOMPLISHMENTS

Current and potential distributions on a disc under conditions of activation polarization were worked out and described in terms of the throwing power parameter, $k/a \left| \frac{\partial \eta}{\partial J} \right|$. Similarly, the distributions were solved for the cylinder-versus-plane electrode configuration for the primary distribution.

PROGRESS IN PAST PERIOD

The cylinder-versus-plane configuration was further analyzed to include the effect of activation polarization on the cylinder. Current distributions were obtained in agreement with the empirical predictions for the system with overpotential effects considered.

Furthermore, experimental measurements were taken on this latter configuration to verify the distributions obtained in the last period. Good agreement between theory and experiment was found for the primary current distribution.

3.3   FOAMING ELECTROLYTE FUEL CELL

Senior Investigator: Dr. L. Nanis

Student: Frank R. McLarnon

OBJECTIVES

The diffusion of reacting species provides an ultimate limitation in all electrochemical processes. For fuel cell applications, dissolved electro-active gases may be rapidly dissolved in a very thin film of electrolyte. Such a structure is provided by a foamed electrolyte and may be useful in practice if the rate of transport is sufficient and the circuit resistance is low. Verification of this possibility is the goal of present laboratory testing of cell geometries, surfactants and electrolytes.

PREVIOUS ACCOMPLISHMENTS

It has been demonstrated that electrode reaction can be supported through a foamed electrolyte.

Work was completed on the design, construction, and testing of a cell which can be readily disassembled and cleaned, and which minimizes migration of oxygen into the anode compartment.

PROGRESS IN PAST PERIOD

Several foam producing compounds have been studied with hydrogen in 4N H_2SO_4 oxidized on platinum (smooth) anodes. Current densities of up to 15 mA/cm^2 have been achieved. Continuous operation for 4 hours resulted in an increase of anode overpotential from 24 to 34 millivolts at a current density of 0.9 mA/cm^2.

3.4 HIGH PERFORMANCE IODINE CATHODE

Senior Investigators:

A. P. Saunders   Dr. H. Wroblowa

OBJECTIVES

To investigate and develop the porous I_2 cathode previously reported under "Primary and Secondary Batteries using Charge Transfer Complexes".

PREVIOUS ACCOMPLISHMENTS

A means was found of obtaining high power densities and high faradaic efficiencies for fuel cell consuming Mg and I_2, by means of a porous cathode; the I_2 being in a concentrated solution and flowed under a pressure gradient through the finely-pored graphite cathode.

PROGRESS IN PAST PERIOD

A current potential relationship has been studied as a function of the pressure gradient across the cathode. The faradaic efficiency at the maximum steady state current at a given pressure is 100% (within the experimental error of± 5%). The power loss at 95% efficiency of I_2 consumption at the cathode is low, the loss increasing with further increase in faradaic efficiency. The design difficulties are discussed. The optimum power density of a Mg I_2 fuel cell is evaluated at 0.3 watts cm^{-2}, the limiting electrode being the metal anode.

4. PUBLICATIONS LIST

PUBLICATIONS LIST

INDEC-1   "The Optimization of MHD Generators with Arbitrary
            Conductivity", H. Yeh and T. K. Chu, ASME Paper
            63-WA-349.

INDEC-2   "The Prediction of Transient Heat Transfer Performance of
            Thermal Energy Storage Devices", M. Altman, D. P. Ross,
            H. Chang, Proceedings of 6th National Heat Transfer
            Conference, Boston, Mass., 1963.

INDEC-3   "The Binary Eutectic as a Thermal Energy Storage System:
            Equilibrium Properties", G. R. Belton and Y. K. Rao, paper
            presented at the 6th National Heat Transfer Conference,
            Boston, Massachusetts, August 11-14, 1963.

INDEC-4   "Theoretical Model of a Thermionic Converter", J. Dunlop
            and G. Schrenk. Proceedings of Thermionic Specialist
            Conference, Gatlinburg, Tenn., pp. 57-62, Oct. 7-9, 1963.

INDEC-5   "Thermophysical and Transport Properties of High Temperature
            Energy Storage Materials", R. Sharma and H. Chang. Paper
            presented at the Third Annual Symposium, High Temperature
            Conversion Heat to Electricity, Tucson, Arizona, Feb. 19-21,
            1964.

INDEC-6   "Solar Collection Limitations for Dynamic Converters-
            Simulation of Solar-Thermal Energy Conversion Systems",
            G. L. Schrenk. Proceedings of AGARD Conference, Cannes,
            France, March 16-20, 1964.

INDEC-7   "Prospects for Thermal Energy Storage", M. Altman. Proceed-
            ings of AGARD Conference, Cannes, France, March 16-20,
            1964.

INDEC-8   "The Hollow Thermionic Converter", L. Zelby, IEEE Annual
            Meeting on Energy Conversion, Clearwater, Florida, May, 1964.

INDEC-9   "The Institute for Direct Energy Conversion", M..Altman. Paper presented at AM. Soc. Eng. Ed. Annual Meeting, University of Maine, Orono, Maine, June 22-26, 1964.

INDEC-10   "Emitter Sheath Polarity in Plasma Diodes", G. Schrenk. Proceedings of Thermionic Specialist Conference, Cleveland, Ohio, October 26-28, 1964, pp. 249-257.

INDEC-11   "Electron Emission from Metals in Gaseous Environment", M. Kaplit, G. Schrenk, L. Zelby. Proceedings of Thermionic Specialist Conference, Cleveland, Ohio, Oct. 26-28, 1964, pp. 4-10.

INDEC-12   "Criteria for Emitter Sheath Polarity in Plasma Diodes", G. Schrenk. Paper presented at ASME Winter Annual Meeting, New York, No. 29, December 3, 1964.

INDEC-13   "An Electrochemical and Microbiological Study of the Formic Acid-Formic Dehydrogenlyase System", R. J. Blasco and E. Gileadi, Advanced Energy Conversion, Vol. 4, pp. 179-186, 1964.

INDEC-14   "Mathematical Simulation of Solar Thermionic Energy Conversion Systems", G. Schrenk and A. Lowi. Proceedings of the International Thermionic Electrical Power Generation Conference, IEEE, London, England, Sept. 20-24, 1965.

INDEC-15   "Cavity Receiver Temperature Analysis", R. McKinnon, A. Turrin, G. Schrenk. AIAA paper No. 65-470, July 26-29, 1965.

INDEC-16   "Electron Emission from Metals in Vapors of Cesium and Fluorine", G. Schrenk and M. Kaplit. Proceedings of the Thermionic Specialist Conference, San Diego, California, October 25-27, 1965.

INDEC-17   "Longitudinal Interaction of Microwaves with an Argon Discharge", C. A. Renton and L. W. Zelby. Applied Physics Letters, Vol. 6, No. 8, pp. 167-169, September 15, 1965.

INDEC-18   "Microwave Interaction with a Non-Uniform Argon Discharge",
L. W. Zelby. Proceedings of the Symposium of Microwave
Interaction with Ferrimagnetics and Plasmas, London, England,
pp. 32-1 to 32-3, September 13-17, 1965.

INDEC-19   "Two-Phase Flow and Heat Transfer for Boiling Liquid Nitrogen
in Horizontal Tubes", M. Altman and J. H. Jones. Chemical
Engineering Progress Symposium Series, Volume 61, No. 57,
October, 1965.

INDEC-20   "Electrical Conductivity of a Partially Ionized Gas in a
Magnetic Field", S. Schweitzer and M. Mitchner.
Physics of Fluids, 10, 799-806 (1967).

INDEC-21   "Models for Electron Emission from Metals with Adsorbed
Monolayers", M. Kaplit, G. L. Schrenk, and L. Zelby.
Advanced Energy Conversion, Vol. 7, pp. 177-189, 1967.

INDEC-22   "Models for Electron Emission from Metals with Adsorbed
Monolayers", M. Kaplit and G. L. Schrenk. Proceedings
of the Twenty-Sixth Annual Conference on Physical Electronics,
Massachusetts Institute of Technology, Cambridge, Mass.,
March 21-23, 1966.

INDEC-23   "Slow Wave Interaction with an Argon Discharge", (Abstract)
L. W. Zelby. Symposium on Properties and Applications of
Low-Temperature Plasmas, XX-th International Congress of
I.V.P.A.C., Moscow, USSR, July 15-18, 1965.

INDEC-24   "Understanding Plasma Diodes and Amplifiers", L. W. Zelby,
Electronic Industries, Vol. 24, No. 11, p. 64, Nov. 1965.

INDEC-25   "A Simplified Approach to the Analysis of Electromagnetic Wave
Propagation Characteristics of Plasma Coated Surfaces",
L. W. Zelby, RCA Review, Vol. 26, No. 4, p. 497, Dec. 1965.

INDEC-26   "Plasma Coated Surface as a Wave Guide", L. W. Zelby.
RCA Engineer, Vol. 11, No. 4, p. 50, January 19, 1966.

INDEC-27   "Measurements of Collision Frequency in an Argon Discharge", L. W. Zelby, W. O. Mehuron, R. Kalagher, Applied Physics Letters, June 15, 1966, Vol. 21, No. 5, pp. 522-524.

INDEC-28   "Effects of Inhomogeneous Electron Density in a Cylindrical Plasma Column Surrounded by a Helix", R. Kalagher. Submitted to IEEE Transactions on Microwave Theory and Techniques, March, 1966.

INDEC-29   "Syringe for Injecting Sodium Potassium Alloy", Samuel Greenhalgh. The Review of Scientific Instruments, Vol. 38, No. 1, pp. 121-122, January, 1967.

INDEC-30   "Characteristics of Plasma Probes in a MHD Working Fluid", A. Whitman, H. Yeh. Proceedings of International Symposium on Magnetohydrodynamic Electrical Power Generation, Salzburg, Austria, July 4-8, 1966, International Atomic Energy Agency, pp. 127-144.

INDEC-31   "Convergence of Successive Approximations to the Scalar Electrical Conductivity of Some Weakly Ionized Real Gases", S. Schweitzer, M. Mitchner, published in the A.I.A.A. Journal, Volume 5, No. 2, pp. 351-353, 1967.

INDEC-32   "The Determination of Thermal Diffusivities of Thermal Energy Storage Materials, Part 1, Solids Up To Melting Point", Han Chang, Manfred Altman, Ram Sharma. Published in the A.S.M.E. Journal, Vol. 89, Series A, #3, pp. 407-414, July, 1967.

INDEC-33   "Electrochemical Principles of Corrosion", Leonard Nanis. Presented at the National Association of Corrosion Engineers Symposium, September, 1966, Philadelphia, Penna.

INDEC-34   "Tolerance Specification by Multiple Alignment Statistics", L. Nanis, presented at Session 14, "Effective Utilization of Grid-Based Interconnection Systems", proceedings of the 1966 Western Electronic Show and Convention, Los Angeles, California, August, I.E.E.E.

INDEC-35 "The Tensor Electrical Conductivity of Atmospheric Cesium-Seeded Argon", S. Schweitzer, A.I.A.A. Journal, Volume 5, No. 5, pp. 844-846 (1967).

INDEC-36 "The Reaction of Molten Metal Droplets with a Rarefied Atmosphere", by M. Altman, D. Ross. Published in the A.I.A.A. Journal, April 1967, Vol. 5, No. 4.

INDEC-37 "Electron Transfer Processes Through Tantalum-Tantalum Oxide Diodes", S. Pollack. Journal of Applied Physics, November, 1966.

INDEC-38 "A Method for Determination of the Permeation Rate of Hydrogen Through Metal Membranes", J. McBreen, W. Beck, L. Nanis. Journal of Electrochemical Society, 113, No. 11, pp.1218-1222 (November, 1966).

INDEC-39 "Tensor Electrical Conductivity of a Partially Ionized Gas in a Magnetic Field", S. Schweitzer and M. Mitchner. Physics of Fluids, 10, 799-806 (1967).

INDEC-40 "New Method of Producing Electric Power by Means of a Thermionic Converter". Patent application by M. Altman.

INDEC-41 "A Metal-Oxide Thin Film Photovoltaic Energy Converter". Patent application by M. Altman and S. R. Pollack.

INDEC-42. "Current and Potential Distribution in Cylindrical Geometries: Engineering Applications", L. Nanis. Submitted to Journal Electrochemical Society. Presented at Current Distribution Symposium, Dallas, May 1967 Meeting, Electrochemical Society.

INDEC-43 "Overpotential-Time Variation for Galvanostatic Charging with Potential Dependent Capacitance", L. Nanis, P. Javet. Journal of The Electrochemical Society, Vol. 114, No. 8, August, 1967.

INDEC-44   "Galvanostatic Charging with Potential Dependent Double Layer Capacitance", L. Nanis, P. Javet. To be submitted to Electrochimica Acta.

INDEC-45   "Decay of Overpotential from the Tafel Region with Potential Dependent Double Layer Capacitance", L. Nanis, P. Javet. To be submitted to Journal of Electrochemical Society.

INDEC-46   "Status of Magnetohydrodynamic Power Generation for Terrestrial Applications", H. Yeh. Presented at the A.I.A.A. Third Annual Meeting in Boston, Massachusetts, Nov. 29 - Dec. 2, 1966. A.I.A.A. Paper 66-1013.

INDEC-47   "First Order Effects of Production on the Continuum Theory of Spherical Electrostatic Probes", Ira M. Cohen and S. Schweitzer. Published in the A.I.A.A. Journal, Vol. 6, No. 2, pp. 298-304, February, 1968.

INDEC-48 .   "The Electric Automobile - A Discussion of Strategy, Tactics, and Leadership", M. Altman. Presented at the National Electric Automobile Symposium, San Jose, California, February 24, 25, 1967.

INDEC-49   "The Electric Automobile - Its Future," M. Altman. Presented at the IEEE International Convention, New York, March 20 - 23, 1967.

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MATERIALS ENGINEERING

APPENDIX

A-1

THERMAL DIFFUSIVITY OF MIXTURES

Senior Investigator: Dr. M. Altman and Dr. K. Sreenivasan

Graduate Student: S. J. Amir

THEORY AND GENERAL METHOD OF APPROACH

In principle the thermal diffusivity of solids can be measured in any apparatus that provides the requisite boundary conditions to the equation for heat conduction in an isotropic material without heat sources and for constant physical properties.

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T$$

where α is the thermal diffusivity defined by

$$\alpha = \frac{K}{\rho C_p}$$

The solution of the equation for transient conduction in a simple geometry will give the thermal diffusivity from the measured temperature distribution as a function of time. The thermal conductivity can then be calculated from a knowledge of the specific heat and density of the solid. Such a method is usually referred to as the "transient" method. It should be noted that no heat flux measurements are necessary.

Steady state methods rely on the solution to the equation

$$\nabla^2 T = 0$$

together with information on the heat flux and temperature at the boundaries. The thermal conductivity is directly obtained in this method. The thermal diffusivity can be calculated from a knowledge of the specific heat and density. Such a method is usually referred to as the "steady state" method.

Accurate determination of heat flux at high temperature is extremely

difficult. Hence, the quasi-method was chosen for the measurement of thermal diffusivity.

The method can be described as follows: Fundamentally the difference between the temperature at the surface and at the center of a cylindrical specimen is measured for a constant rate of surface temperature rise. The thermal diffusivity is then calculated using the diameter of the specimen, the rate of rise of the surface temperature and the temperature difference. The boundary condition on which this method is based can be easily realized experimentally. No heat flux need be measured. This is a tremendous advantage as accurate measurement of heat flux at high temperatures is very difficult. The mathematical details of this method are given in references 1 and 2.

Thermal Diffusivity of Mixture Samples

In the void fraction of two constituent species A and B are v_A and v_B the thermal diffusivity of the composite sample can be predicted only if its thermal conductivity and the specific heat per unit volume are known. The composite specific heat per unit volume can be obtained by

$$(\rho C_p)_T = v_A (\rho C_p)_A + v_B (\rho C_p)_B \tag{1}$$

ρ - Density - $lbs/c.ft$ v_A void fraction of A

C_p Specific heat - $BTu/lB\ °F$ v_B void fraction of B

    Subscript   T - composite

       A - Species A

       B - Species B

In the case of thermal conductivity of the composite one can only calculate the upper and lower bounds. The two bounds are given by

$$k_{T_1} = v_A k_A + v_B k_B \tag{2}$$

$$k_{T_2} = \frac{k_A k_B}{v_A k_A + v_B k_B} \tag{3}$$

The bounds can be improved from a knowledge of statistical correlation functions of the mixture samples. The aim of this proposed investigation is to determine the correlation functions experimentally and study how to improve the above mentioned bounds

Thermal Diffusivity of Porous Samples

In this case one of the constituents is gas and its properties have to be used in the equations (1), (2) and (3). If the material can be considered structurally as a solid matrix with isolated pores the thermal conductivity is given to a first order approximation as .

$$K_T = \nu_s K_s + \nu_p \left(K_g + 4 E \sigma d_p T^3 \right) \tag{4}$$

where subscripts s, p and g refer to the solid, pore and gas, respectively and

E – Total emissivity of the inside surface of the pore

T – Absolute temperature

d_p – width of the cavity

The above equation is obtained by considering that the gas in pore does not participate in the radiation transfer of heat. It is the purpose of this investigation to recast the above formula assuming that the gas participates in the radiation heat transfer.

Making the Specimen

In the previous investigation on solid specimens no difficulty was experienced in obtaining them. The Lucalox samples were bought, and the LiF samples were made by melting LiF sample in a carbon mold heated by high frequency eddy currents in an induction furnace. However, it is difficult to buy samples with a definite porosity or a mixture sample of different ratio of the constituent species.

EXPERIMENT:

The experimental program consisted of preparing samples of aluminum oxide, magnesium oxide, titanium oxide and zirconium oxide. The main

interest was for aluminum oxide since its conductivity and emissivity are well established. Titanium oxide, besides aluminum oxide was also found amenable to specimen fabrication. Magnesium oxide was, however, found very hard to work with while there was partial success with zirconium oxide.

All samples were prepared by incorporating Napthelene powder in the oxide powder. Just before use Napthelene powder was passed through a screen with opening of 0.42 MM. This would induce uniformity of the pore diameter. The mixture of oxide and Napthelene was then mixed with organic liquid binder. The liquid binders were metal resinates with metal content up to 10%.

The aggregate of binder, Napthelene and Metal oxide was then pressed in a die at a pressure of 3200 PSI. For Aluminum and Zirconium the die was 2" diameter while for Titanium and Magnesium it was $2\frac{5}{8}$ ". The bigger diameter size used was to account for the shrinkage taking place in those oxides. After pressing, the samples were dried for an extended period of time at $70-80^{\circ}$c until no Napthelene odor could be noticed. The samples were then fired at 1280°c in air for about 24 hours so that the organic material carbonizes and the metal from the resinate should form its respective oxide.

The pure oxide sample now is fired in vacuum at temperatures 80% of the melting point of the metal oxides for four or five hours in standard manner. After firing, polished sections were examined which showed that pores were roughly sperical or ellipsoidal in shape. Samples (2" dia. and $1\frac{1}{2}$" deep) with up to 65% porosity were successfully made.

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TRANSIENT TEMPERATURE RESPONSE OF CYLINDRICAL, COMPOSITE ENERGY STORAGE DEVICES

M. Altman, Director

K. Sreenivasan, Post Doctoral Fellow

This paper describes an analysis of the transient temperature response of cylindrical, composite energy storage devices whose thermal conductivity, density and specific heat are independent of temperature. Solutions are presented for a three-layer composite cylinder with heat fluxes specified at the inner and the outer faces. _The conventional method of separation of variables is used. It is shown that the customary weighting function η for the Bessel functions, has to be modified to η, $\dfrac{\alpha_1 k_2}{\alpha_2 k_1}\eta$, $\dfrac{\alpha_1 k_3}{\alpha_3 k_1}\eta$ respectively for the three layers to make the eigenfunctions orthogonal in the region considered. Expressions are derived for the amount of energy available for storage and efficiency of storage.

The geometry of the system considered is described in Fig. 1. The composite cylinder receives heat from outside and this heat is conducted inwards to the core where it is utilized. In this process it heats up the intermediate storage material. The storage material has to be properly sheathed and increase in its enthalpy during any interval is a measure of the energy available for storage.

Conceptually, the physical analogue would correspond to a situation where the regions (1) and (3) would be sheathing material containing the energy storage material in region (2). The inner core will contain the energy conversion devices and the outer surface of region (3) will receive heat from outside.

The aim of this analysis is to determine the following:

(1) The optimun geometry for the device

(2) The influence of the thermal conductivity, thermal diffusivity specific heat and density of the various layers, on the over all performance

(3) Variation of temperature and heat flux at every point in the device.

To demonstrate the method of analysis it was decided to consider a four-layered composite cylinder. The following assumptions were made.

(1) Heat flow in the radial direction only.

(2) Perfect thermal contact at the interfaces.

(3) Physical properties do not vary with temperature.

(4) No internal heat generation.

(5) The material in the four layers is isotropic and homogeneous.

The boundary conditions considered in this analysis are for the case where the heat fluxes at the inner and outer boundaries of the composite cylinder are specified.

This is usually the case in practice where the heat fluxes are specified and one wants to predict the corresponding variation. The following dimensionless variables are employed.

$$\eta = \frac{r}{d} \; ; \qquad \theta = \frac{\alpha_3 t}{d^2} \qquad T_i(\eta, \theta) = \frac{T_i^*(r,t)}{T_0}$$

where i=1, 2 and 3 for the three regions. In terms of these variables the governing equations are

$$\frac{\partial T_1}{\partial \Theta} = \frac{\alpha_1}{\alpha_3} \nabla^2 T_1 \quad ; \qquad \frac{a}{d} \leq \eta \leq \frac{b}{d}$$

$$\frac{\partial T_2}{\partial \Theta} = \frac{\alpha_2}{\alpha_3} \nabla^2 T_2 \quad ; \qquad \frac{b}{d} \leq \eta \leq \frac{c}{d}$$

$$\frac{\partial T_3}{\partial \Theta} = \nabla^2 T_3 \quad ; \qquad \frac{c}{d} \leq \eta \leq 1$$

with the initial condition at $\Theta = 0$, $\quad T_1(\eta, 0) = T_2(\eta, 0) = T_3(\eta, 0) = 0$

and the boundary conditions $\quad \eta = \frac{a}{d} \; ; \quad \frac{\partial T_1}{\partial \eta} = \frac{q_1 d}{T_0 k_1} \cdot$

$$\eta = 1 \; ; \quad \frac{\partial T_3}{\partial \eta} = \frac{q_2 d}{T_0 k_3}$$

The matching conditions at the interface are given by

$$\eta = \frac{b}{d} \; ; \qquad T_1\left(\frac{b}{d}, \Theta\right) \cdot = \quad T_2\left(\frac{b}{d}, \Theta\right)$$

$$\frac{k_1}{k_2} \frac{\partial T_1}{\partial \eta} = \frac{\partial T_2}{\partial \eta}$$

$$\eta = \frac{c}{d} \; ; \qquad T_2\left(\frac{c}{d}, \Theta\right) = T_3\left(\frac{c}{d}, \Theta\right)$$

$$\frac{k_2}{k_3} \frac{\partial T_2}{\partial \eta} = \frac{\partial T_3}{\partial \eta}$$

Unavailability of space prevents us from presenting the details of the solution. They are found in Reference 1. The final solution can be written for the three regions as

$$T_1(\eta, \Theta) = A\left(\Theta + \frac{\alpha_3}{\alpha_1} \frac{\eta^2}{4}\right) + B_1 \ln \eta + C_1 + \sum W_n \, Exp(-\mu_n^2 \Theta) \cdot X_{1n}(\eta)$$

$$T_2(\eta, \Theta) = A\left(\Theta + \frac{\alpha_3}{\alpha_2} \frac{\eta^2}{4}\right) + B_2 \ln \eta + C_2 + \sum W_n \, Exp(-\mu_n^2 \Theta) \, X_{2n}(\eta)$$

$$T_3(\eta, \Theta) = A\left(\Theta + \frac{\eta^2}{4}\right) + B_3 \ln \eta + C_3 + \sum W_n \, Exp(-\mu_n^2 \Theta) \, X_{3n}(\eta)$$

where

$$A = \frac{\frac{2 q_2 d}{k_3 T_0}\left(1 - \frac{q_1}{q_2} \frac{d}{a}\right)}{\frac{k_2 \alpha_3}{k_3 \alpha_2}\left(\frac{c^2}{d^2} - \frac{b^2}{d^2}\right) + \frac{k_1 \alpha_3}{k_3 \alpha_1}\left(\frac{b^2}{d^2} - 1\right) + \left(1 - \frac{c^2}{d^2}\right)}$$

$$B_1 = \frac{\frac{q_1 d^2}{k_1 a T_0}\left\{\frac{k_2 \alpha_3}{k_3 \alpha_2}\left(\frac{c^2}{d^2} - \frac{b^2}{d^2}\right) + \frac{k_1 \alpha_3}{k_3 \alpha_1}\left(\frac{b^2}{d^2}\right) + 1 - \frac{c^2}{d^2}\right\} - \frac{q_2 d}{k_3 T_0} \frac{\alpha_3}{\alpha_1}}{\frac{k_2 \alpha_3}{k_3 \alpha_2}\left(\frac{c^2}{d^2} - \frac{b^2}{d^2}\right) + \frac{k_1 \alpha_3}{k_3 \alpha_1}\left(\frac{b^2}{d^2} - 1\right) + \left(1 - \frac{c^2}{d^2}\right)}$$

$$B_2 = \frac{\frac{q_2 d}{k_3 T_0}\left\{\frac{k_1 \alpha_3}{k_2 \alpha_1}\left(\frac{b^2}{d^2} - 1\right) - \frac{\alpha_3}{\alpha_2} \frac{b^2}{d^2}\right\} + \frac{q_1 d^2}{k_2 a T_0}\left\{\frac{k_2 \alpha_3}{k_3 \alpha_2} \frac{c^2}{d^2} + 1 - \frac{c^2}{d^2}\right\}}{\frac{k_2 \alpha_3}{k_3 \alpha_2}\left(\frac{c^2}{d^2} - \frac{b^2}{d^2}\right) + \frac{k_1 \alpha_3}{k_3 \alpha_1}\left(\frac{b^2}{d^2} - 1\right) + \left(1 - \frac{c^2}{d^2}\right)}$$

$$B_3 = \frac{\frac{v_1 d^2}{k_3 a T_0} + \frac{v_2 d}{k_3 T_0}\left\{\frac{k_2 \alpha_3}{k_3 \alpha_2}\left(\frac{c^2}{d^2} - \frac{b^2}{d^2}\right) + \frac{k_1 \alpha_3}{k_3 \alpha_1}\left(\frac{b^2}{d^2} - 1\right) - \frac{c^2}{d^2}\right\}}{\frac{k_2 \alpha_3}{k_3 \alpha_2}\left(\frac{c^2}{d^2} - \frac{b^2}{d^2}\right) + \frac{k_1 \alpha_3}{k_3 \alpha_1}\left(\frac{b^2}{d^2} - 1\right) + \left(1 - \frac{c^2}{d^2}\right)}$$

$$C_1 = \frac{1}{\left(2\frac{a^2}{d^2} - \frac{b^2}{d^2}\right)}\left\{\frac{\alpha_1 k_3}{\alpha_3 k_1}\left[g_3(1) + C_3\right] - \frac{a^2}{d^2}\left[\frac{\alpha_3}{\alpha_1}\frac{A}{4}\frac{a^2}{d^2} + 2B_1 \ln \frac{a}{d}\right] + \frac{c^2}{d^2}\left[\left(\frac{\alpha_1 k_2}{\alpha_2 k_1} - \frac{\alpha_1 k_3}{\alpha_3 k_1}\right)g_3\right.\right.$$

$$\left.\left. + \left(\ln \frac{c}{d}\right)\left(B_2 \frac{\alpha_1 k_2}{\alpha_2 k_1} - B_3 \frac{\alpha_1 k_3}{\alpha_3 k_1}\right) + \left(\frac{\alpha_1 k_2}{\alpha_2 k_1}C_2 - \frac{\alpha_1 k_3}{\alpha_3 k_1}C_3\right)\right]\right\}$$

$$C_2 = C_1 - \ln\frac{b}{d}(B_2 - B_1) - \frac{A}{4}\frac{b^2}{d^2}\left(\frac{\alpha_3}{\alpha_2} - \frac{\alpha_3}{\alpha_1}\right)$$

$$C_3 = C_2 + \ln\frac{c}{d}(B_2 - B_3) + \frac{A}{4}\frac{c^2}{d^2}\left(\frac{\alpha_3}{\alpha_2} - 1\right)$$

$$W_n = \frac{1}{\mu_n^2 M_n}\left(\frac{\alpha_1}{\alpha_3}\right)\left(\frac{d}{k_1 T_0}\right)\left[\frac{a}{d}v_1 X_{1n}\left(\frac{a}{d}\right) - v_2 X_{3n}(1)\right]$$

and μ_n's are zeros of the secular determinant in the equation

$$\begin{bmatrix} J_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\frac{a}{d}\right) & Y_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\frac{a}{d}\right) & 0 & 0 & 0 & 0 \\ J_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\frac{b}{d}\right) & Y_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\frac{b}{d}\right) & -J_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{b}{d}\right) & -Y_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{b}{d}\right) & 0 & 0 \\ \sqrt{\frac{\alpha_2}{\alpha_1}}\frac{k_1}{k_2}J_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\frac{b}{d}\right) & \sqrt{\frac{\alpha_2}{\alpha_1}}\frac{k_1}{k_2}Y_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\frac{b}{d}\right) & -J_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{b}{d}\right) & -Y_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{b}{d}\right) & 0 & 0 \\ 0 & 0 & J_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{c}{d}\right) & Y_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{c}{d}\right) & -J_0\left(\mu_n\frac{c}{d}\right) & -Y_0\left(\mu_n\frac{c}{d}\right) \\ 0 & 0 & \sqrt{\frac{\alpha_3}{\alpha_2}}\frac{k_2}{k_3}J_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{c}{d}\right) & \sqrt{\frac{\alpha_3}{\alpha_2}}\frac{k_2}{k_3}Y_1\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\frac{c}{d}\right) & -J_1\left(\mu_n\frac{c}{d}\right) & -Y_1\left(\mu_n\frac{c}{d}\right) \\ 0 & 0 & 0 & 0 & J_1(\mu_n) & Y_1(\mu_n) \end{bmatrix}\begin{bmatrix} A_{1n} \\ B_{1n} \\ A_{2n} \\ B_{2n} \\ A_{3n} \\ B_{3n} \end{bmatrix} = 0$$

and

$$X_{1n}(\eta) = A_{1n} J_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\eta\right) + B_{1n} Y_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_1}}\eta\right); \quad \frac{a}{d} \le \eta \le \frac{b}{d}$$

$$X_{2n}(\eta) = A_{2n} J_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\eta\right) + B_{2n} Y_0\left(\mu_n\sqrt{\frac{\alpha_3}{\alpha_2}}\eta\right); \quad \frac{b}{d} \le \eta \le \frac{c}{d}$$

$$X_{3n}(\eta) = A_{3n} J_0(\mu_n\eta) + B_{3n} Y_0(\mu_n\eta); \quad \frac{c}{d} \le \eta \le 1$$
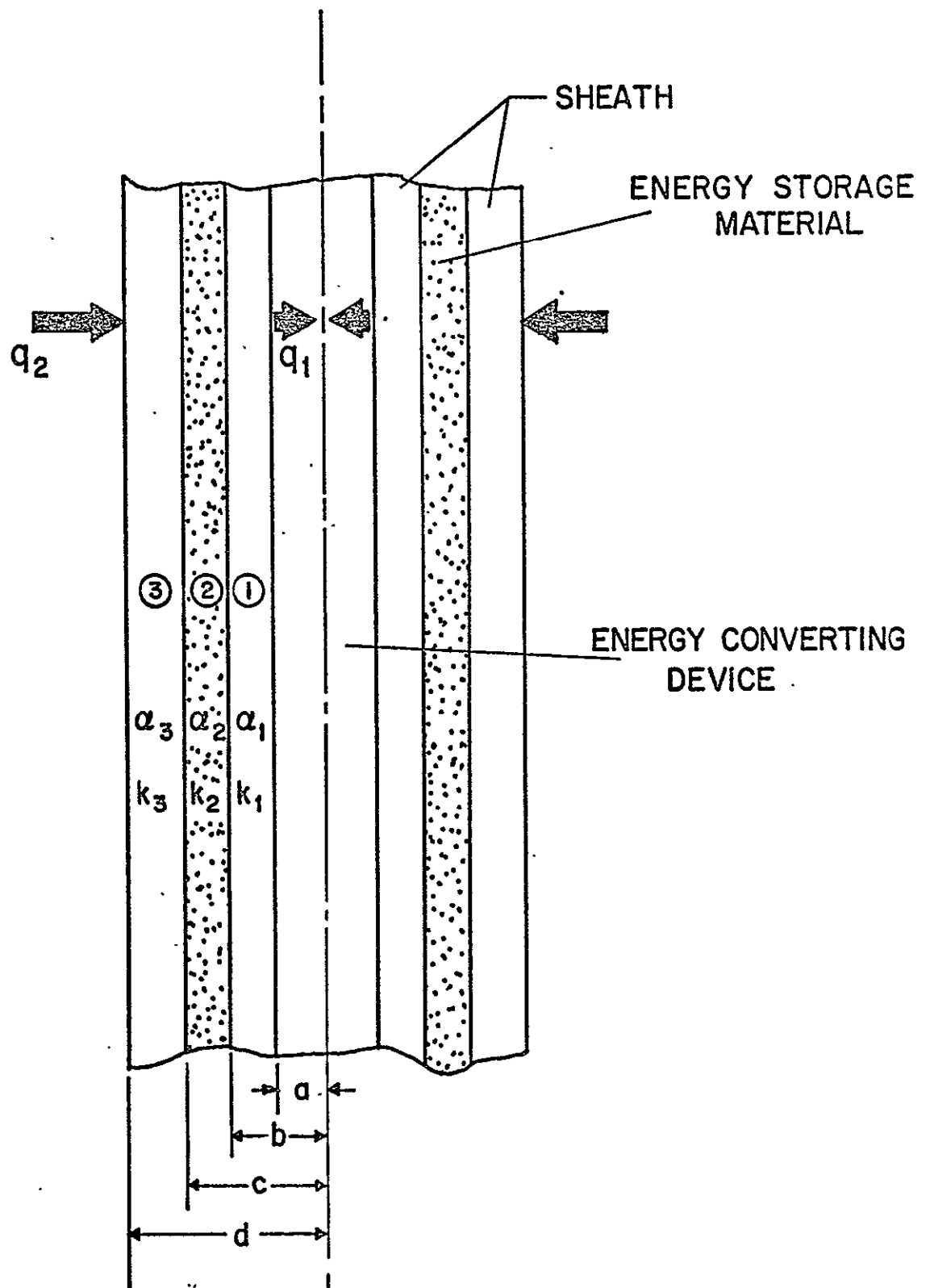
Fig.1 Mathematical model of the thermal energy storage device .

The temperature variation at the inner surface is obtained by substituting $\eta = \dfrac{a}{d}$ in equation (5a). The heat flux is given by

$$F_1 = \frac{k_1 T_0}{d}\frac{\partial T_1}{\partial \eta} \qquad \frac{a}{d} \leq \eta \leq \frac{b}{d}$$

$$F_2 = \frac{k_2 T_0}{d}\frac{\partial T_2}{\partial \eta} \qquad \frac{b}{d} \leq \eta \leq \frac{c}{d}$$

$$F_3 = \frac{k_3 T_0}{d}\frac{\partial T_3}{\partial \eta} \qquad \frac{c}{d} < \eta \leq 1$$

where the temperature derivatives can be obtained by differentiating equations (5). Another parameter of interest is the total heat energy available for storage. This is given by the difference in heat flux crossing the interfaces $\eta = \dfrac{c}{d}$ and $\eta = \dfrac{b}{d}$.

$$F^* = \frac{k_2 T_0}{d}\left\{ \left[\frac{\partial T_2}{\partial \eta}\right]_{\eta=\frac{c}{d}} - \left[\frac{\partial T_2}{\partial \eta}\right]_{\eta=\frac{b}{d}} \right\}$$

where the derivatives are calculated as indicated earlier. As F* represents a rate let us now obtain the total energy. If the system is in the bright period for a time t_0 the energy per unit area impinging on the outside is

$$E_{in} = q_2 t_0 = \frac{q_2 d^2}{\alpha_3}\theta_0$$

Total energy available for storage is given by

$$E_{storage} = \int_0^{t_0} F^* dt = \frac{d^2}{\alpha_3}\int_0^{\theta_0} F^* d\theta$$

or

$$E_{storage} = \frac{k_2 T_0 d}{\alpha_3}\int_0^{\theta_0}\left\{ \left[\frac{\partial T_2}{\partial \eta}\right]_{\eta=\frac{c}{d}} - \left[\frac{\partial T_2}{\partial \eta}\right]_{\eta=\frac{b}{d}} \right\} d\theta$$

To assess the performance of the storage device it is convenient to define a storage efficiency by the ratio, $E_{storage}/E_{in}$ or

$$\eta_{storage} = \frac{k_2 T_0}{q_2 d}\frac{1}{\theta_0}\int_0^{\theta_0}\left\{ \left[\frac{\partial T_2}{\partial \eta}\right]_{\eta=\frac{c}{d}} - \left[\frac{\partial T_2}{\partial \eta}\right]_{\eta=\frac{b}{d}} \right\} d\theta$$

This analysis clearly demonstrates how all the relevant parameters of thermal storage device can be calculated. The great advantage of this method of analysis lies in the fact that no horrendous inversions are involved and that all the calculations, though painstaking, are possible.

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<u>P L A S M A   E N G I N E E R I N G</u>

APPENDIX

A-2

THERMOELECTRIC PROPERTIES OF GRAPHITE COMPOUNDS

Principal Investigator: L. A. Girifalco

Post-doctoral Fellow: S. Sachidanandam

Graduate Student: T. Montelbano

PREPARATION

The barium-graphite compound C_8Ba has been synthesized by diffusion anneal. The optimum condition for preparation of this new compound is heating barium and pyrolytic graphite in vacuum at $575^{\circ}C$ for 400 hours. At higher temperatures the formation of barium carbide competes for available barium and yields an inhomogeneous composite. At a lower temperature, $500^{\circ}C$ for example, there is approximately 50% less compound formation after 1600 hours of anneal.

STRUCTURE

The lattice parameters of C_8Ba have been determined by Debye-Sherrer techniques. The use of thin walled capillaries allowed for all X-ray work to be performed in vacuum. In the "a"-direction the parameter of C_8Ba is $2.49\overset{\circ}{A}$ while that measured for the pyrolytic graphite used is $2.45\overset{\circ}{A}$. The distance between carbon layers in the "c"-direction is $5.28\overset{\circ}{A}$ for compound and $3.35\overset{\circ}{A}$ for graphite.

Macroscopically the expansion along the c-axis is manifest by a doubling of height. No apparent change is noted in the a-direction. It is important to note that mechanical integrity of the compound is maintained upon formation.

ELECTRONIC PROPERTIES

Resistivity measurements have been performed in vacuum in the temperature range from room temperature to 600°C. Preliminary results are shown in Figure 1.
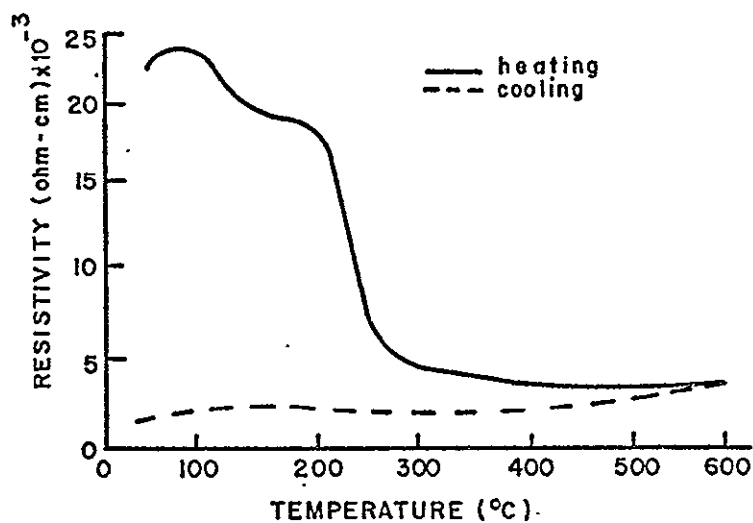

Figure 1. Resistivity of C_8Ba in temperature range
from room temperature to 600°C.

The transition from semi-conducting to metallic type behavior makes this compound very interesting for electronic study. Changes in resistivity are attributed to a loss of barium from the C_8Ba. This would involve the formation of less concentrated compounds and concurrent structure alterations. Work is continuing to elucidate these changes.

Investigation of thermoelectric properties in the same temperature range is planned.

ELECTROCHEMICAL ENGINEERING

APPENDIX

A-3

CURRENT AND POTENTIAL DISTRIBUTION IN CYLINDRICAL
GEOMETRIES: ENGINEERING APPLICATION TO FUEL CELL DESIGN

Senior Investigator: Dr. L. Nanis

Graduate Student: Wallace Kesselman

By means of the bilinear transformation of coordinator, the cylinder-plane configuration can, by suitable choice of constants of the transformation, be reduced to one of concentric circles for which, as demonstrated last quarter, the current distributions can be solved and expressed in the original geometry in terms of simple analytical expressions. This method has been extended to the case where overpotential exists. In this latter case, after transformation of coordinates, the LaPlace equation must be solved by separation of variables, and the results obtained in this geometry must then be made to correspond to the cylinder-wall geometry. The results obtained can be compactly plotted as front-to-back-face ratio of current densities, and are shown in Fig. 1 as a function of throwing power parameter.

The expression for the primary current distribution on the cylinder in this geometry

$$J/J_{ave} = \frac{p^2/a^2 - 1}{p/a + \sin\theta}$$

where p = distance from wall to center of cylinder

a = radius of cylinder

θ = angular position on cylinder as measured from the horizontal in a counter-clockwise direction

was verified by means of an experiment in which one wall of a pan with vertical walls was made as electrode whose counter-electrode was a glass pipe with nickel foil wrapped around it, leaving a gap for a segment insulated from the main electrode. Current was then measured through this segment. Agreement was achieved as shown in Figures 2 and 3.
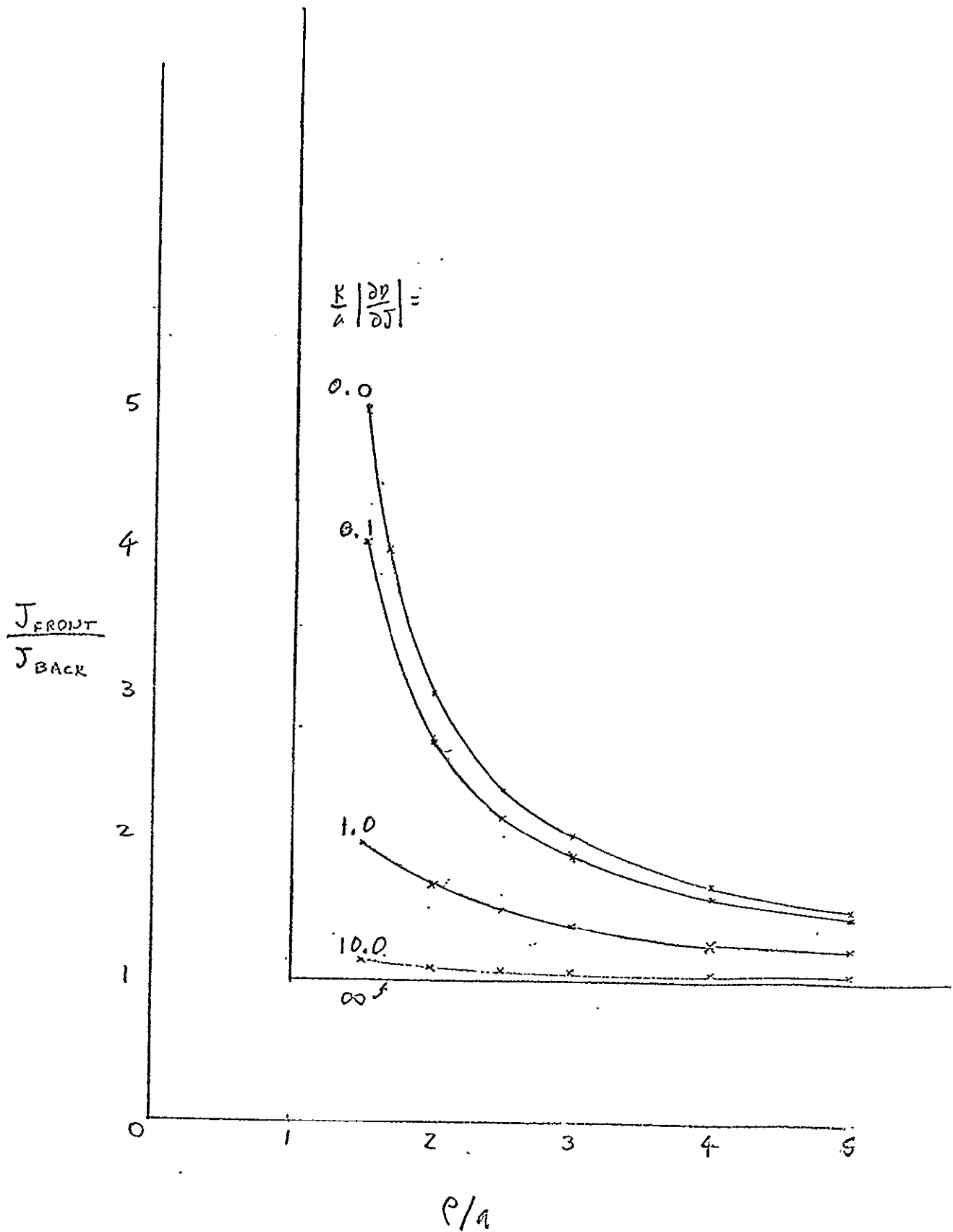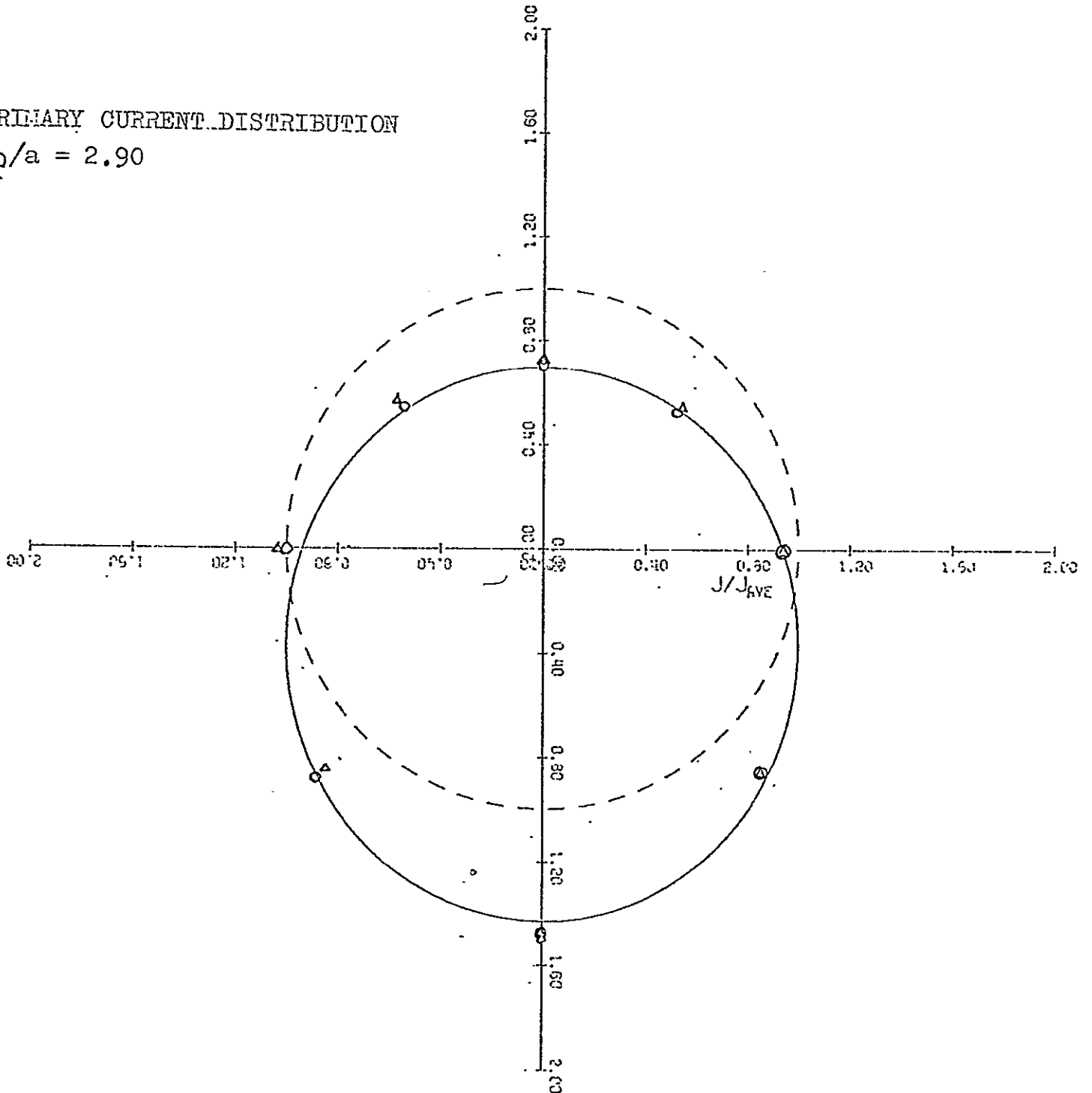
Fig. 1

A3-2 .

Fig. 2

PRIMARY CURRENT DISTRIBUTION

$\rho/a = 2.90$

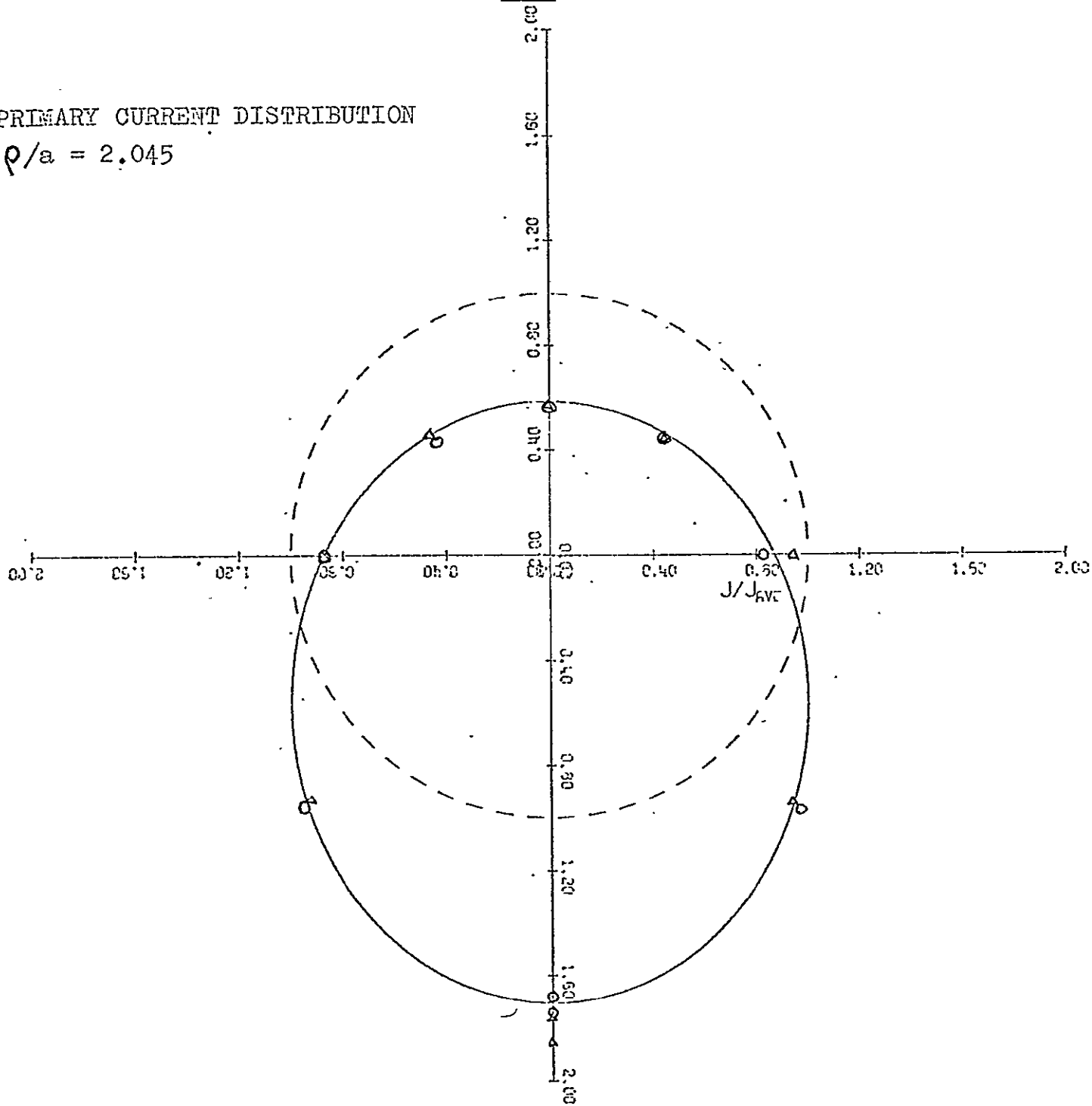PRIMARY CURRENT DISTRIBUTION
$\rho/a = 2.045$

J/J_{ave}

Fig. 3

A3-4

FOAMING ELECTROLYTE FUEL CELL

Senior Investigator: Dr. L. Nanis

Student: Frank R. McLarnon

The improved design foam fuel cell (see Sec. 3.3 INDEC SR-14, June, 1968) has been used for anodic oxidation studies of hydrogen in $4N$ H_2SO_4 on bright, smooth platinum electrodes. The addition of 0.1 weight percent GAFAC RE-610 to the electrolyte sustained currents larger than the 0.6 mA/cm^2 associated with vigorous stirring by hydrogen bubbles. This was taken as evidence of participation of the RE-610 additive in the reaction for totally immersed electrodes. The foam produced in this way permitted a higher current density (3 mA/cm^2) to be reached before excessive polarization due to diffusion limitation. Studies of GAFAC RE-610 were discontinued because the unwanted side reactions involving the additive masked true foam structure effects on the limiting current density. The experience with GAFAC RE-610 prompted studies of background currents in foams produced by various additives for stirring by helium. In addition, electrolyte with and without additives was studied for behavior of the current-overpotential relation for several stirring conditions produced by regulating the hydrogen flow rate. Equal currents for solution with and without additive (for the same stirring condition) were taken as an indication of non-participation by the additive. As a futher check, current-overpotential curves for the liquid phase stirred by helium alone clearly demonstrated the absence of hydrogen reaction, since the region of oxygen overpotential was reached when the current density exceeded 0.05 mA/cm^2 i.e., much less than the liquid phase hydrogen limiting current density of 0.6 mA/cm^2 for comparable stirring. With the above background tests, as a guide, electrolyte foamed by the addition of 0.1 wt. percent Textilana FM 1001 permitted the attainment of a limiting current of 15 mA/cm^2.

Preliminary life tests with this additive have shown a 2 mV/hr increase of anode overpotential after 4 hours of operation at 0.9 mA/cm^2, chosen to correspond to an initial polarization of 24 mV.

HIGH PERFORMANCE IODINE CATHODE

A. P. Saunders   Dr. H. Wroblowa

The previously reported power densities for the porous I_2/I^- electrode were underestimated. The main sources of error were due to air-locks in the back of the electrode and leaks around the electrode periphery, which prevented higher currents to be obtained at a high faradaic efficiency.

The leaks have been a major retarding factor in this work due to the incompatibility of most materials with iodine. Graphite is the only material found to date suitable for the cathode, and two sealing materials, E7 epoxy resin and RTV 60 silicon rubber have been used. The electrode (Fig. 1) has been used successfully for 13 days at a mean current density of over 200 ma/cm^2 [*]. Examination showed that only the epoxy resin was visibly attacked, but this did not affect the cathode performance.

This cathode is made of FC50 porous graphite (Pure Carbon Co.) with micro pores predominately in the 0.3 - 2 range (median pore $\emptyset = 0.8$), and is combined with a Mg anode in a fuel cell. The oxidant is supplied to the porous cathode under pressure, and the current-potential characteristics are measured using model 610a and 150b Keithley electrometers and model #680 Moseley recorders.

Results

Flow-rate measurements were carried out using an 0.2 cm thick and 1 cm diameter graphite membrane. The flow rate, v, was measured by a decrease in height of the meniscus of (0.973 mI$_2$ in 2.5 m KJ) solution in a glass tube from which the electrolyte was pushed through the electrode under a pressure (Δp). The change of height of the meniscus (Δh) was measured using a cathetometer. The time (Δt) was measured using a stop watch. The accuracy of the measurement was ~2.5%. Faradaic efficiency was calculated

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[*] Maximum current densities in excess of 1A/cm^2 have been drawn for periods of hours.

by comparing the observed flow rate with the simultaneously measured maximum constant current obtainable at the given Δp over a period of time. The efficiency was 100 ± 3% (i.e. ∼100% within the experimental error).

The current-overpotential relationship was recorded in steady state as a function of applied pressure. At each Δp value, there is only one point on the I^- curve corresponding to the condition

$$I_{max} \approx 2F\, v\, C_o$$

where I is the current and C_o is the concentration of I_2 in the supplied electrolyte, v is the flow-rate. At lower currents a part of non-reduced I_2 passes into the solution at a rate measured by the value of (I max - I).

Discussion

The current-potential relationship is shown in Fig. 2 in form of plots of reduced current, $\dfrac{i}{i\,max}$, versus the cathode overpotential. The points seem to lie on the same curve for $\dfrac{i}{i\,max} > 0.9$. This result is not predicted by theoretical analysis which would indicate an increase with the pressure gradient of the overpotential η corresponding to the given $\dfrac{i}{i\,max}$ value. However, for the range of ∇p values studied, this increase may be within the limits of the experimental error. The numerical results of the theoretical analysis are being completed.

On the basis of the results obtained, it may be anticipated that upon further increase of the pressure gradient, the increase of the cathode over-voltage corresponding to ≈95% I_2 consumption will not be very high.

The power density of the Mg-I_2 fuel cell obtainable in practical arrangement can now be projected. The power density, P, is given by

$$P = [\, V_{I_2}^{o} - V_{Mg} + \eta\, I_2 - i\,R\,]\, i$$

where V_{Mg} (at higher current densities) is approximately given by [1]

$$V\,Mg = -1.45 + 1.67\,i$$

1 W. N. Carson, W. H. Fischer, E. G. Siwek, Electrochem. Technology, 5, 423, 1967.

where $V_{I_2} = 0.535$ v, η_{I_2} (at 95% efficiency) ≈ -0.35 V, $R \approx 0.45$ Ω (specific resistivity of the solution is 4.5 Ω cm, distance between electrodes - 0.1 cm).

Then

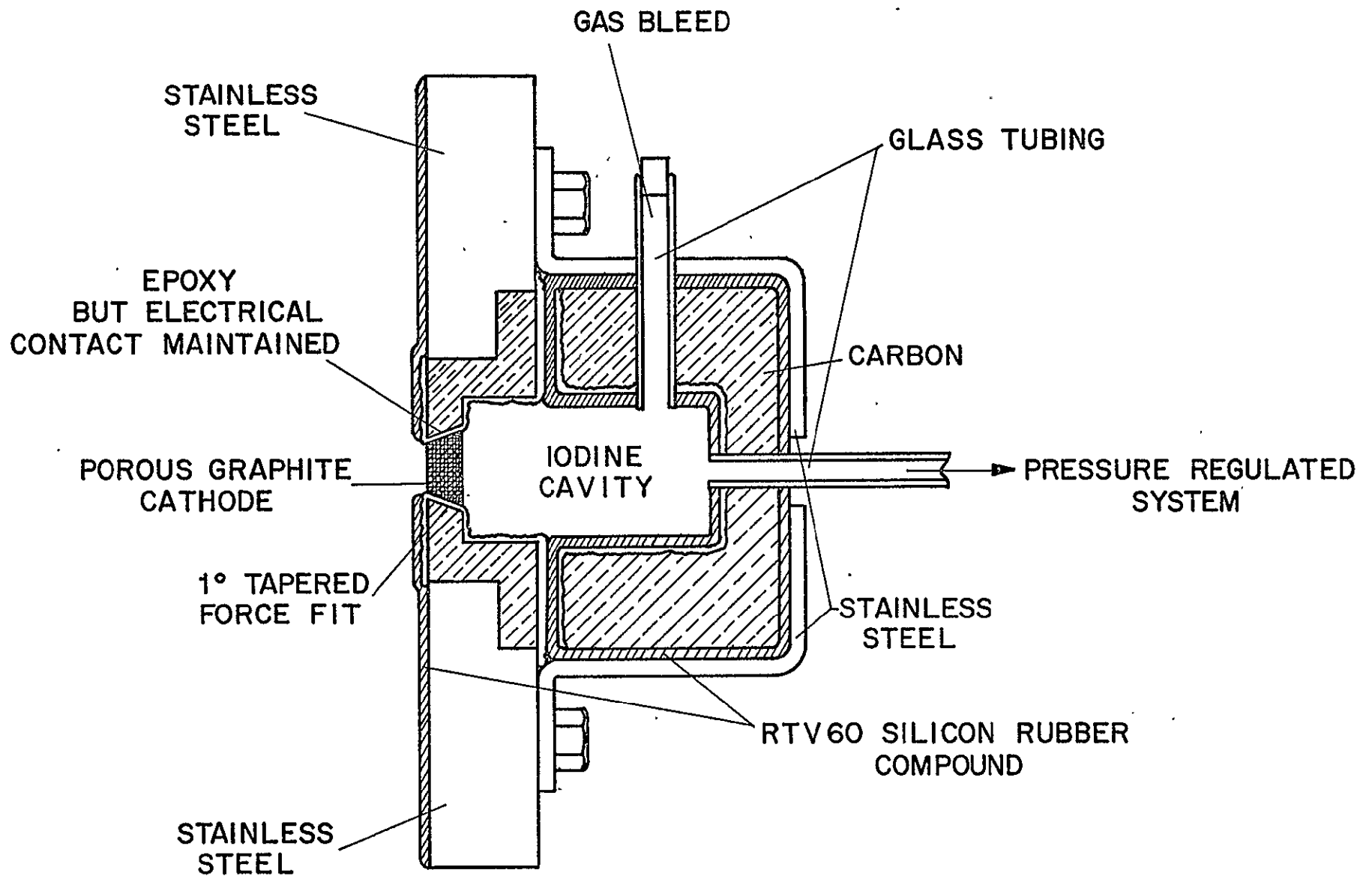$$P_{(95\% \text{ eff})} \approx [\, 1.6 - 2.12 \, i \,] \, i \qquad (1)$$

and the maximum power density is obtained at $i \approx 0.38$ A/cm^2. The pressure gradient corresponding to this value is easily found from equation 1 combined with the condition $i = 0.95 \, i_{\text{max}} = 0.95 \cdot 2F \, v \, C_o \, \nabla p$, where v is the flow rate at $\nabla p = 1 \frac{\text{atm}}{\text{cm}} \approx 2.2 \times 10^{-6}$ 1/sec, $C_o = 1$ M, is the initial concentration of I_2 and ∇p is the pressure gradient.

Then

$$\nabla P_{\text{opt}} \approx 0.9 \text{ atm/cm}$$

The performance of the cell is limited mainly by polarization of the metal anode, which accounts for the major part of the power loss, and is the limiting factor of the cell operation. On the other hand, the power losses due to the cathode operating at about 0.95% efficiency of iodine consumption are small.

In absolute values, the maximum power density of the operating cell can be projected at $P = 0.3$ watts/cm^2. Further improvement would involve 1) decrease of the anode polarization, 2) decrease of the IR drop in the electrolyte.
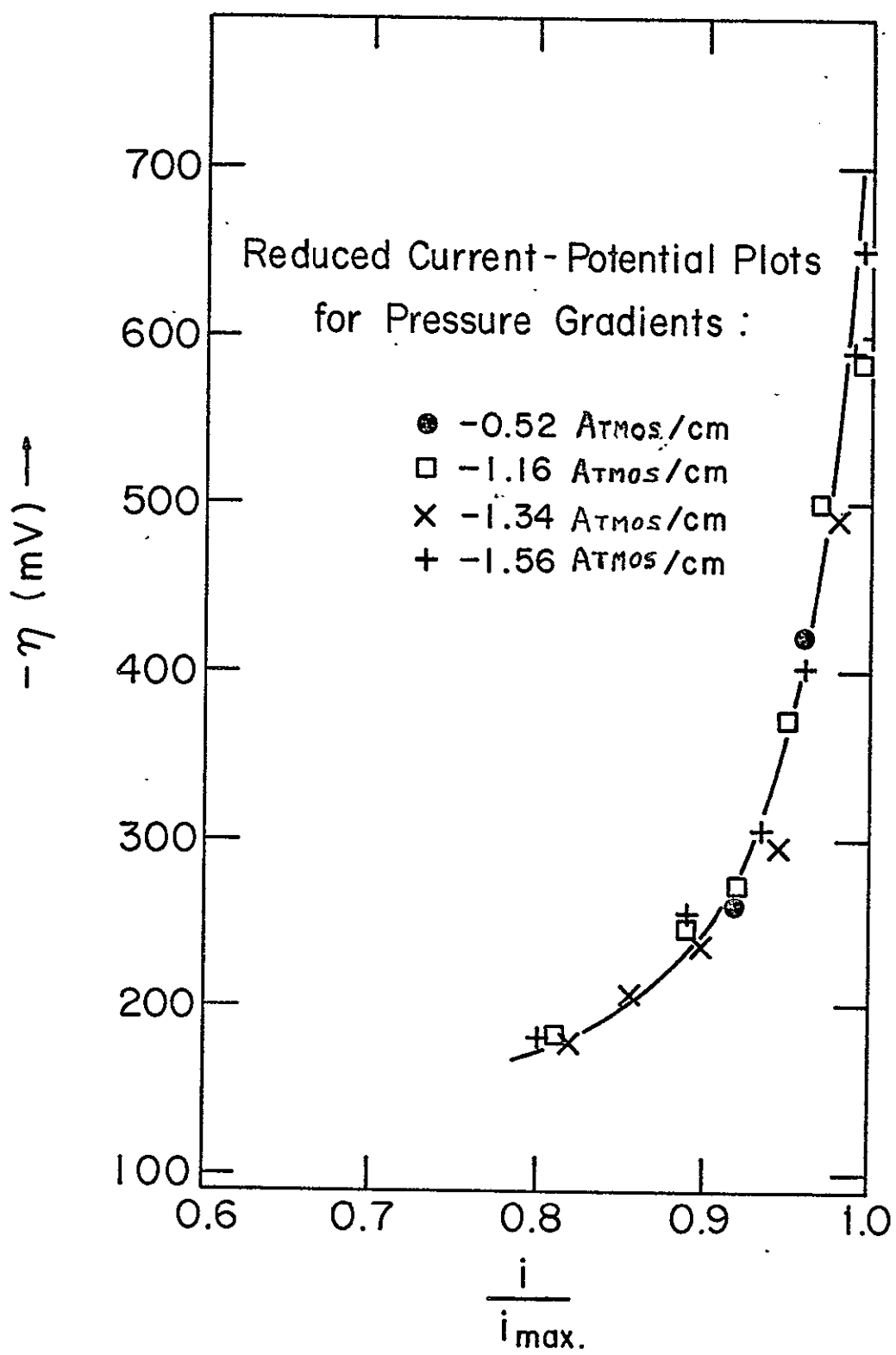
Figure 1

Figure 2